PB84-171545

Study of the Effectiveness of a Catalytic Combustion Device on a Wood Burning Appliance

Battelle Columbus Labs., OH

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

Mar 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-171545

EPA-600/7-84-046
March 1984

STUDY OF THE EFFECTIVENESS OF A CATALYTIC COMBUSTION DEVICE ON A WOOD BURNING APPLIANCE

by

John M. Allen, William H. Piispanen,
and Marcus Cooke
Battelle Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Contract Number 68-02-3169
Work Assignment 30

Project Officer

Michael C. Osborne
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Prepared for:

Office of Research and Development
U.S. ENVIRONMENTAL PROTECTION AGENCY
Washington, DC 20460

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/7-84-046	2.	3. RECIPIENT'S ACCESSION NO. PB84 171545
4. TITLE AND SUBTITLE Study of the Effectiveness of a Catalytic Combustion Device on a Wood Burning Appliance		5. REPORT DATE March 1984 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) John M. Allen, William H. Piispanen, and Marcus Cooke		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle-Columbus Laboratories 505 King Avenue Columbus, Ohio 43201		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-02-3169 Task 30
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Task Final; 6/82 - 12/83 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Michael C. Osborne, Mail Drop 65, 919/541-4113.

16. ABSTRACT The report gives results of operating a wood stove, incorporating a catalytic combustor, while burning air-dried oak at low burning rates. Gas composition was measured continuously both at the entrance of the catalyst (after the gases had left the burning wood) and at the exit of the stove (after the gases had traversed the catalyst). These continuous monitors showed a reduction of about 3:1 in volatile hydrocarbons measured by a flame ionization detector, and a comparable reduction in carbon monoxide. These monitors showed no significant corresponding reduction when the active catalyst was replaced with an identical ceramic element, but without the noble metal coating. Grab samples collected from the flue gas early during the wood burning cycle, analyzed by direct gas-phase MS and GC, confirmed the lower concentrations of volatile combustible species when the active catalyst was used. Integrated samples of flue gas collected throughout the test burn were analyzed for less volatile organic species and PAH species. These analyses indicated that the catalyst was less effective in reducing these species, including particulate collected on a hot filter and high molecular weight species such as BaP.

17. KEY WORDS AND DOCUMENT ANALYSIS					
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group		
Pollution	Exhaust Gases	Pollution Control	13B	21B	
Wood	Carbon Monoxide	Stationary Sources	11L	07B	
Stoves	Dust	Wood Stoves	13A	11G	
Catalytic Converters		Particulate	07A, 13I		
Catalysis	Aerosols		07D		
Hydrocarbons			07C		
18. DISTRIBUTION STATEMENT Release to Public		19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 47		
		20. SECURITY CLASS (This page) Unclassified	22. PRICE		

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

A wood stove with a catalytic combustor incorporated within the stove was operated while burning air dried oak at low burning rates. Gas composition was measured continuously both at the entrance of the catalyst where the gases had left the burning wood, and at the exit of the stove where the gases had traversed the catalyst. These continuous monitors showed approximately a 3:1 reduction in volatile hydrocarbons as measured by a flame ionization detector, and a comparable reduction in carbon monoxide. These monitors showed no significant corresponding reduction when the active catalyst was replaced with an identical ceramic element to which the noble metal catalytic coating had not been applied.

Grab samples collected from the flue gas early during the wood burning cycle were analyzed by MS and GC, and confirmed the lower concentrations of volatile combustible species when the active catalyst was used.

Integrated samples of flue gas collected throughout the test burns were analyzed for less volatile organic species and PAH species. These analyses indicated that the catalyst was less effective in reducing these species, including particulate collected on a hot filter and high molecular weight species such as BaP.

CONTENTS

Abstract iii
Figures v
Tables vi
Acknowledgement vii

1. Introduction 1
2. Description of Test Methods 2
   - Sampling Methods and Equipment 2
   - Test Procedures 5
   - Post-Test Procedures 5
   - Grab Sample Collection and Analysis 6
   - GC/MS Analyses 6
   - Data Reduction 7
3. Test Results 8
   - Continuous Sampling 8
   - Emission Factors 8
   - NO_x Emissions 8
   - Grab Sample Results 13
   - Results of Total Organics Determinations 13
   - Results of PAH Analyses 20
4. Discussion of Test Results 24
   - Effect of Stove Operation on Combustion 24
   - Catalyst Performance 26
   - Effect of Catalytic Action on THC and CO Emission 26
   - Effect of Catalyst on NO_x 35
   - Effect of Catalyst on Volatile Gases 35
   - Effect of Catalyst on Condensibles and Particulate 35
5. Recommendations for Future Test Programs 37

References 38

FIGURES

Number		Page
1a	Schematic diagram of catalytic stove	3
1b	Schematic diagram of sampling system	4
2	Emission factors, active catalyst Run 4	10
3	Emission factors, active catalyst Run 5	11
4	Emission factors, inactive catalyst Run 6	12
5	NO emissions Run 5	14
6	NO_x emissions Run 5	15
7	NO emissions Run 6	16
8	NO_x emissions Run 6	17
9	Characterization of samples by boiling point range	19
10	Total Ion chromatogram of flue gas	21
11	Excess air and flue gas temperatures	25
12	Temperature within active catalyst	27
13	Hydrocarbon emission rates with active catalyst	28
14	THC vs. CO correlation for gases entering catalyst	30
15	THC vs. CO correlation for gases leaving stove	31
16	THC vs. CO correlation for gases leaving stove with inactive catalyst	32
17	Carbon monoxide emission factors correlated with catalyst temperatures	33
18	Hydrocarbon emission factors correlated with catalyst temperatures	34

TABLES

Number		Page
1	Operating Conditions for Stove Tests	9
2	Results of Modified Method 5 Sampler	9
3	Average Flue Gas Analysis	9
4	Volatile Flue Gas Composition	18
5	Total Measured Organic Emissions	20
6	Individual PAH Compounds (g/m^3)	22
7	Recovery Standard Data (d_{12}-BaP)	23
8	Benzo(a)pyrene Results from Catalytic Wood Stove Study	23
9	Particulate and Organic Emissions	36

ACKNOWLEDGEMENTS

The authors would like to thank the U.S. Environmental Protection Agency and the EPA Project Officer, Michael C. Osborne, who supported this study under Contract 68-02-3169 (Task 30). The consultation of Tom Parker and Gary Yee (California Air Resources Board) who were technical advisors to the program is also gratefully acknowledged.

Battelle technical staff who assisted in this study included Harry Leonard and William Baytos (Sampling); Warren Bresler (Laboratory Procedures); Cheng C. Chuang, Timothy Hayes, and Robert Iden (Mass Spectrometry).

SECTION 1

INTRODUCTION

The increased use of catalytic combustion devices on wood-burning appliances has raised a number of concerns regarding the emissions from these sources into residential areas. The purpose of this study was to determine the effectiveness of catalytic combustors in reducing emissions of hydrocarbons and CO, and also to determine the species of compounds which are emitted during the operation of a typical catalytic-equipped appliance. The stove used in this program had a honeycomb, ceramic catalytic device, referred to as a catalyst, internally within the stove.

While the catalyst is believed to be effective in the promotion of combustion, actual operation had not been thoroughly characterized with respect to stove operating variables. Of particular concern to this study were the following:

- Operating conditions where the catalyst is most effective in reducing emissions.
- Effectiveness of the catalyst in low burn-rate operation.
- Combustion products formed in the catalytic combustion process.

For this program a catalytic-equipped wood-burning appliance was tested in the Battelle combustion research laboratory. Continuous samples of the combustion gases before and after the catalyst were analyzed by on-line gas analyzers for O_2, CO_2, CO, THC, NO, and NO_x. Temperatures at various points in the gas stream and also within the catalyst bed were monitored during the test. A sampling train (EPA Method 5 type) with a packed column of XAD-2 resin was used to collect particulate and vapor phase organics from the gas stream. A grab sample of combustion gas leaving the stove was taken for analysis of low molecular-weight species (100 amu) by direct mass spectrometry and selective gas chromatographic analysis.

On-line gas analyses indicate that the catalytic device is effective in reducing both total hydrocarbons (THC) and carbon monoxide (CO) at temperatures where the catalyst is active (above approximately 425 C (800 F)). At lower temperatures there is less effect on THC emissions. When a blank catalyst, i.e., ceramic substrate without the noble metal coating, was used in place of the active catalyst, there was a noticeable decrease in the catalyst temperature, and the emission levels increased.

SECTION 2

DESCRIPTION OF TEST METHODS

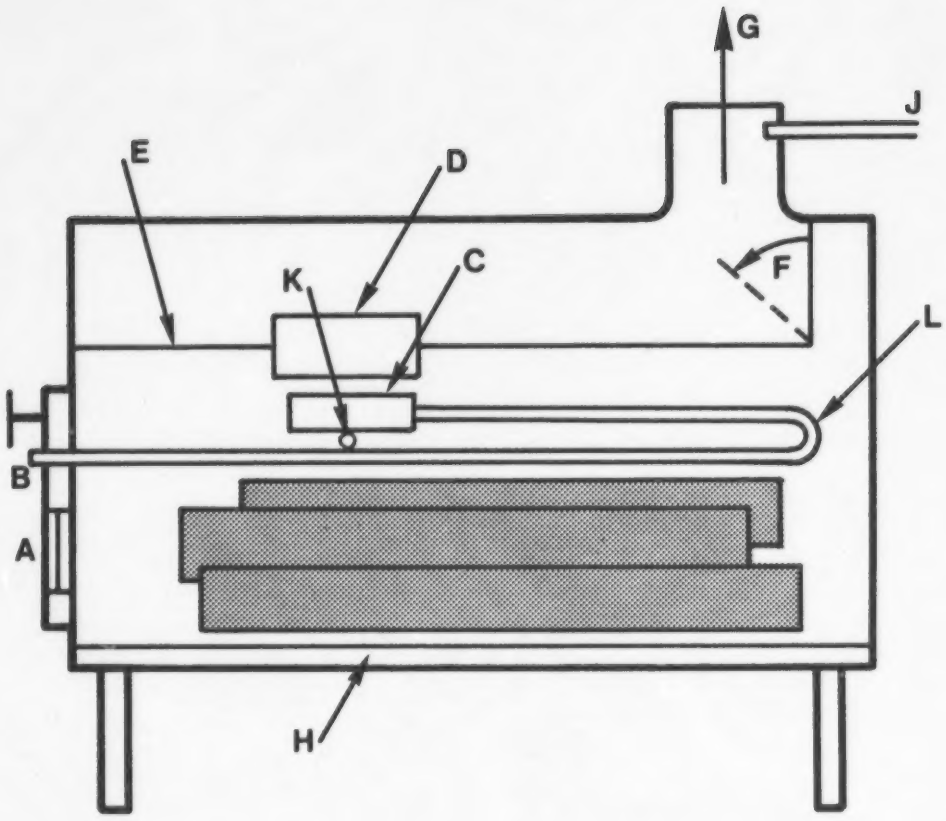
A test program was conducted at the Battelle-Columbus' Combustion Test Facility to provide an evaluation of a catalytic combustor equipped, wood burning appliance. A Webster Oak stove was installed in the facility, and with the catalyst operating, the stove was conditioned for 100 hours by burning split white oak and pine. During these burns, the controls were adjusted in order to obtain effective burning at low wood consumption rates. The catalyst (both normal and uncoated) was supplied by the Corning Glass Works. It utilized a 1/4 inch (0.6 cm) square honeycomb ceramic substrate 3 inch (7.5 cm) thick and 6 inch (15 cm) diamter. Figures 1a and 1b are schematic diagrams of the stove and laboratory installation.

Sampling Methods and Equipment

Aspirated thermocouples and rake-type sample probes were installed in the stove to sample combustion gas entering the catalyst (primary) and the combustion gas in the flue (secondary). Thermocouples were mounted to monitor (1) secondary air temperature inside the air duct located within the combustion chamber, (2) several stove skin temperatures, (3) stack wall temperature, (4) sample train temperatures, and (5) ambient air temperature. Also, the viewing window located over the catalyst was replaced with a fitted insert which permitted vertical traversing of the catalyst to measure temperatures within the catalyst bed. During the preliminary burns, the point of maximum temperature was determined in the catalyst and the bare thermocouple was then locked at that point.

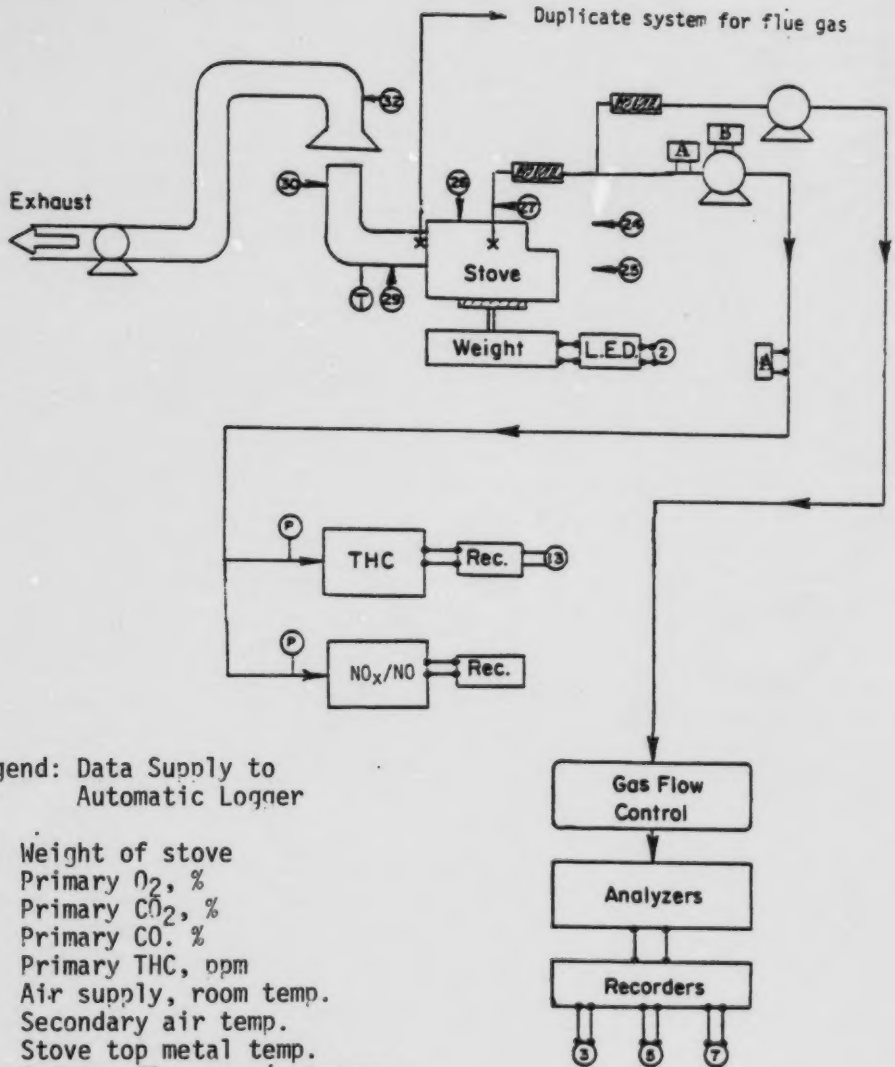
The test facility was designed to provide continuous sampling and monitoring of various stove parameters as illustrated in Figure 1b. The data collection and processing system is limited to collecting single point data, and due to limitations on data storage, most tests were designed for 110 scans at 2-minute intervals (total time, 220 minutes).

Not shown in the test facility schematic drawing, is the NO/NO_x system used during this program. To measure both NO and NO_x in the primary and secondary combustion zone, emissions would have required a total of four instruments and an excessive total sample volume. As an alternative, a timer box was designed for this program which cycled the NO and NO_x modes of the Beckman 955 chemiluminescent analyzer on 5-minute intervals. The Beckman instrument includes switching solenoids which are activated by the timer. The instrument output signal was recorded on a dual pen recorder which tracked both NO and NO_x modes. A heated line was used for NO/NO_x sampling since this heated line also supplied samples to the THC analyzers, a control



A Primary air supply, with controls in door
B Secondary air supply, with no controls
C Secondary air distributor
D Ceramic catalytic element
E Baffle
F Baffle bypass, opens when loading door is open
G Exhaust to chimney
H Ceramic hearth
J Gas sample probe for gas leaving stove
K Gas sample probe for primary combustion products entering catalyst
L Distribution pipe, heating secondary air supply

FIGURE 1a. Schematic Diagram of the Catalytic Stove



Legend: Data Supply to Automatic Logger

2	Weight of stove
3	Primary O_2, %
5	Primary CO_2, %
7	Primary CO. %
13	Primary THC, ppm
24	Air supply, room temp.
25	Secondary air temp.
26	Stove top metal temp.
27	Primary flue gas (entrance to catalyst)
29	Base of chimney, temp.
30	Top of chimney, temp.
32	Exhaust hood, temp.
A	Primary gas sample time, temp.
B	Primary gas pump, temp.

FIGURE 1b. Schematic Diagram of Sampling System.

valve was installed at the instrument sample inlet to control sample flow and pressure at designated span values.

This program included a total of six test burns. During five of the six tests, a sample for volatile gas analysis was taken at a point near the gas exit to the chimney by drawing a sample into a preevacuated 3-liter glass bulb. Also during monitoring, flue gas samples were taken continuously from the stack at a point 75 cm above the flue entrance into the insulated stack. For condensible organics an extractive sampler similar to an EPA Method 5 train was used with the addition of a packed column of XAD-2 resin following the heated filter. This train includes a glass-lined sampling probe which is sealed into the flue, a heated filter holder, 200 C (390 F) fitted with a fiberglass filter, an XAD-2 resin adsorption chamber at 20 C (68 F), a series of ice cooled scrubbers, a drying cartridge filled with silica gel, suitable gas flow monitoring and gas moving devices which complete the collection train.

Test Procedures

Tests were conducted by first starting a fire in the appliance using red oak splits. During this time the sampling equipment was equilibrated and leak checked, monitoring instruments were zeroed and spanned. The data acquisition program was initiated by recording instrument and sample codes in the data system, wood type and moisture, barometric pressure, scan interval, test duration, start time, weight and type of wood charge, and test title. Also, sample pump and line heaters were turned on to allow system conditioning.

After the initial wood charge had burned to glowing coals the bed was raked flat and the electronic scale zeroed. A preweighed charge of wood was placed in the combustion chamber at exactly 1 minute prior to data acquisition with the primary setting at air full open. All analyzers were then checked to verify that flow rates and line pressures were within specified limits.

Upon initiation of data acquisition the continuous sampler was started. The stove operator monitored catalyst temperature using a digital readout. When the catalyst temperature reached 425 C (800 F) the primary air supply was adjusted to a predetermined set point. This time delay was normally less than 5 minutes. At no other time through the duration of a burn was the air readjusted or fuel added to the stove. Data acquisition and extractive sampling continued until the predetermined termination time was reached.

Post-Test Procedures

After sampling was complete, the extractive sampling system was removed from the stack and all openings capped with clean aluminum foil. The system was then transported to a chemistry laboratory for recovery according to the wood stove sampling protocol.[1] Analyzers were all purged with N_2 gas and then post-test zero and span checks were made to determine instrument drift or malfunction during testing.

Grab Sample Collection and Analysis

A special sampling port was fabricated for grab samples, and was located approximately 30 cm from the stove outlet. The sample duct made a 90 degree bend approximately 15 cm on center above the stove and the sample point was approximately 15 cm beyond this point. The sample point was capped off when not in use. A stainless steel probe extended through the sample port sleeve and terminated 9 cm past the sleeve so samples were withdrawn from the center of the flue.

Clean 3 liter glass sample bulbs were evacuated to approximately 10^{-6} torr pressure and heated to remove residual material. The sample bulbs each contained a stopcock, and 12/30 standard taper joint which fit the mass spectrometer and gas chromatograph inlet systems.

Samples were taken 15 minutes after the start of a burn, and approximately 20 seconds were required to fill the 3 liter sample flask. After sampling, the glass bulbs were taken to the Battelle Gas Mass Spectrometry Laboratory for analysis.

Samples were analyzed using a combination of mass spectrometry and three gas chromatographic techniques. A Consolidated Electrodynamics Corporation, Model 21-620 mass spectrometer was used for a general analysis from mass 2 to 100. Since the mass spectrometer does not separate carbon monoxide and nitrogen, carbon monoxide was determined using an Aerograph, Model 202, gas chromatograph with a molecular sieve column and a thermal conductivity detector.

Low molecular weight hydrocarbons and sulfur gases were determined using a Varian, Model 3700, gas chromatograph. Hydrocarbon analysis employed a Poropak Q column and flame ionization detector, and sulfur gases were separated on a Supelco S column and detected with a flame photometric detector. The samples were analyzed for sulfur gases the same day they were sampled to prevent reactive degradation.

GC/MS Analyses

Three determinations can be made on the Modified Method 5 sample; condensible organics, particulate matter, and PAH. The Method 5 sampling train separates the sample into a particulate fraction in the heated probe and filter section, and a semivolatile organics fraction which collects on the resin. The resin material is extracted with methylene chloride along with the particulate-laden filter in a Soxhlet extractor. The filter is re-extracted separately to remove PAH compounds not extracted by methylene chloride. After extractions are complete, the front filter is carefully removed from the Soxhlet cup, dried, and weighed to determine the total amount of particulate matter collected during the run. The resin-filter extract is combined with the extracted aqueous impinger samples to produce a combined organics sample. The combined extract is analyzed by gas chromatography and gravimetry to determine condensible organics. This extract is also used for PAH analyses.

The filter/resin extraction yields two extracts: a methylene chloride extract which contains most of the organic burden, and a benzene extract (filter only) which contains many of the PAH species. The combined extracts are reduced to a convenient volume by a Kuderna-Danish concentrator. The PAH fraction is reduced to about 1 ml by use of a Kuderna-Danish concentrator and to a final volume to 0.5 ml by directing a gentle stream of nitrogen across the top of the sample. An internal standard (9-phenylanthracene) is spiked into the extract at this point.

The analytical scheme involves a glass capillary GC/MS procedure which separates many of the PAH isomers (including benzo(a)pyrene and benzo(e)pyrene) with only one chromatographic run. A 30 m SE-54 capillary column is directly coupled to the mass spectrometer via a glass capillary transfer line. The gas chromatograph is equipped with a Grob-type injector enabling splitless injections. The column is temperature programmed from 160-320 C at 4 C/min. Injector temperature is 300 C while the transfer line is held at 315 C. Compounds such as coronene and dibenzopyrenes with boiling points above 520 C are eluted as sharp peaks. Close to baseline separation is achieved for isomeric compounds such as phenanthrene/anthracene, benzo(a)-anthracene/chrysene and benzo(a)pyrene/benzo(e)pyrene.

The GC/MS system used for PAH analysis consists of a Finnigan Model 9500 biomedical type gas chromatograph coupled with a Finnigan Model 3200 mass spectrometer. Data collection and processing is handled by a Finnigan Incos Data System which utilizes a Data General Nova 3 computer with 32K of memory.

Data Reduction

The stored results from data acquisition were transferrd to a magnetic tape following the conclusion of each test. For the NO/NO_X data, strip charts were marked for identification. The data were later transferred to a graphics data tape, during which time, tabular columns of stored data were hard copied. Raw data were processed into hard copy graphics using the Tektronix Plot 50 program. Data from NO/NO_X strip charts were entered into the laboratory notebook and then transferred into the Tektronix Plot 50 system. As a result, tests 2 through 6 produced the following data: (1) a series of instantaneous printouts of real-time and engineering data as collected during the test, (2) tabular columns of selected real and calculated data over the total test duration, (3) graphic representations of 12 operating parameters as a function of time, and (4) selected parametric plot representations.

SECTION 3

TEST RESULTS

The test program was designed to include six stove tests. Of these tests, five were conducted with the normal catalyst in place and one test, Number 6, was run using a ceramic substrate without the coating of catalytic material. Tests were designed for medium to low burn rates and run as close to reproducible conditions as possible, except Test 3, which was conducted with a lower rate of primary air. All tests used four pieces of wood, together weighing about 10 lb (4.54 kg).

Continuous Sampling

Stove operating data for tests 2 through 6 are included in Table 1. The operational data for the Modified Method 5 tests are included in Table 2. Note that Modified Method 5 tests and grab samples were taken only on Tests 2, 3, 4, and 6. Test No. 5 was not sampled for organics. Continuous gas analyses were conducted at locations before and after the catalyst. The data was recorded every 2 minutes and then averaged over the entire test. The results are presented in Table 3. The first test was considered a shake-down run, and useable data was not obtained.

In Test 2 and 3 problems in the gas sample transport systems prevented determination of valid average flue gas parameters for the entire test. Grab sample analyses were taken for combustion gas analysis in all tests.

Emission Factors

The test results were compiled using the Battelle Wood Stove Data Reduction Program. These results were then presented graphically using a Techtronix Plot 50 Program. The emission factors for CO and THC as lbs/1000 lb of wood burned are presented in Figures 2, 3, and 4. In these representations, the effect of secondary combustion in the catalyst on CO and THC emissions can be observed.

NO_x Emissions

Continuous sampling of flue gases from both stove locations (primary before catalyst--secondary after the catalyst) was conducted for NO and NO_x emissions. The gas monitoring measurements were made at 5 minute intervals. The 5 minute intervals were averaged using a computational graphic technique and the data were entered into a laboratory log book. Combustion gas values were corrected to 0 percent oxygen (O_2), and entered into a display program for graphic presentation. The results of the comparative plots for NO and NO_x

TABLE 1. OPERATING CONDITIONS FOR STOVE TESTS

Test No.	Weight of Wood		Average (actual) Burn Rate		Average Catalyst Temp.		Average Stack Temp.		Condition
	lbs	Kg	lb/hr	Kg/hr	F	C	F	C	
2	10.0	4.5	3.5	1.6	941	505	364	184	High air
3	9.4	4.3	2.4	1.1	775	413	343	173	Low Air
4	10.4	4.7	2.6	1.2	919	493	376	191	Med. air
5	10.4	4.7	2.3	1.0	898	418	349	176	Med. air
6	10.2	4.6	2.1	1.0	676	358	318	154	Uncoated Catalyst

TABLE 2. RESULTS OF MODIFIED METHOD 5 SAMPLES

Test No.	Volume Sampled		Sample Time	Flue Gas Moisture	Average Filter Temp.		Particulate Emissions*	
	(dscf)	(dscm)	(min.)	(percent H_2O)	(F)	(C)	(gr/dscf)	(g/dscm)
2	99.85	2.83	135	6.7	407	208	0.0130	0.0298
3	109.17	3.08	191	6.0	405	207	0.0256	0.0586
4	131.15	3.71	310	4.9	410	210	0.0268	0.0613
6	120.53	3.41	219	3.3	406	208	0.0186	0.0426

* Corrected to 12 percent CO_2

TABLE 3. AVERAGE FLUE GAS ANALYSIS

Test No.	O_2 (percent)		CO_2 (percent)		CO (percent)		THC (ppm)		PAH,** (mg/m^3)
	Primary	Secondary	Primary	Secondary	Primary	Secondary	Primary	Secondary	Secondary
2	11.2	17.4*	9.0	3.0*	0.9	0.1*	4320	1135*	3.4
3	13.4	--	6.7	--	--	--	2922	1001	3.4
4	12.7	17.3	7.6	3.4	0.7	0.1	5089	2184	2.0
5	13.8	15.8	7.2	5.0	0.7	0.2	4029	1279	--
6	12.1	16.3	8.1	4.2	0.8	0.5	3550	3186	3.2

* Averaged only over last 105 minutes of test run. Early secondary readings not valid during Test No. 2.
** From Table 6.

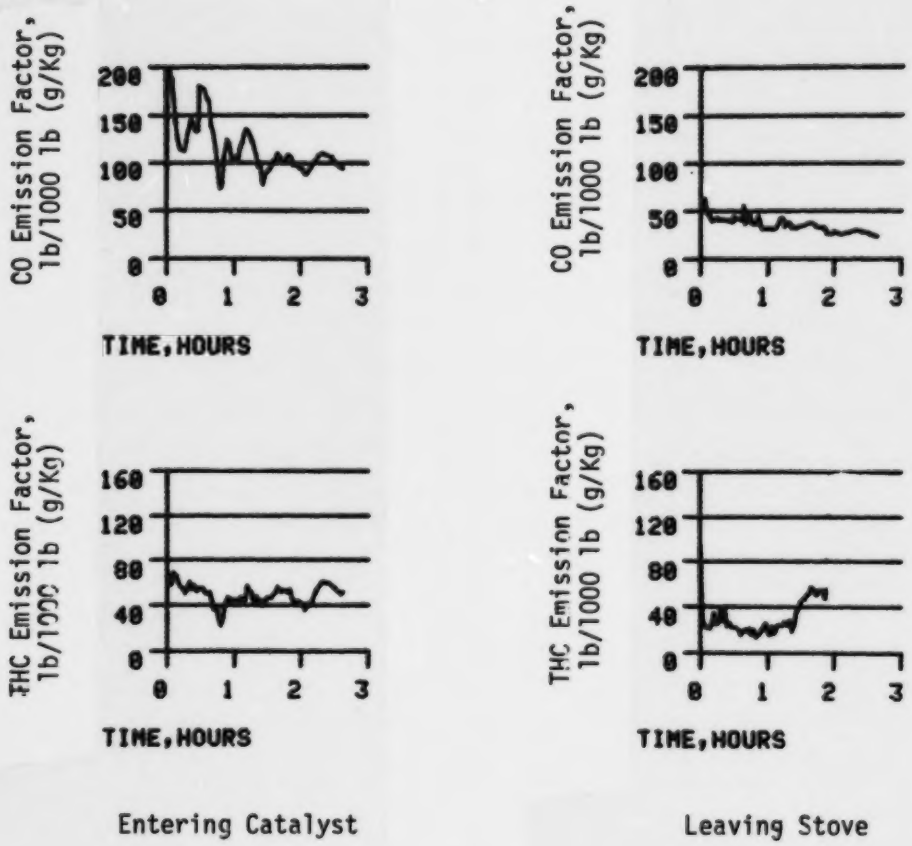


FIGURE 2. Emission Factors with Active Catalyst-Test 4

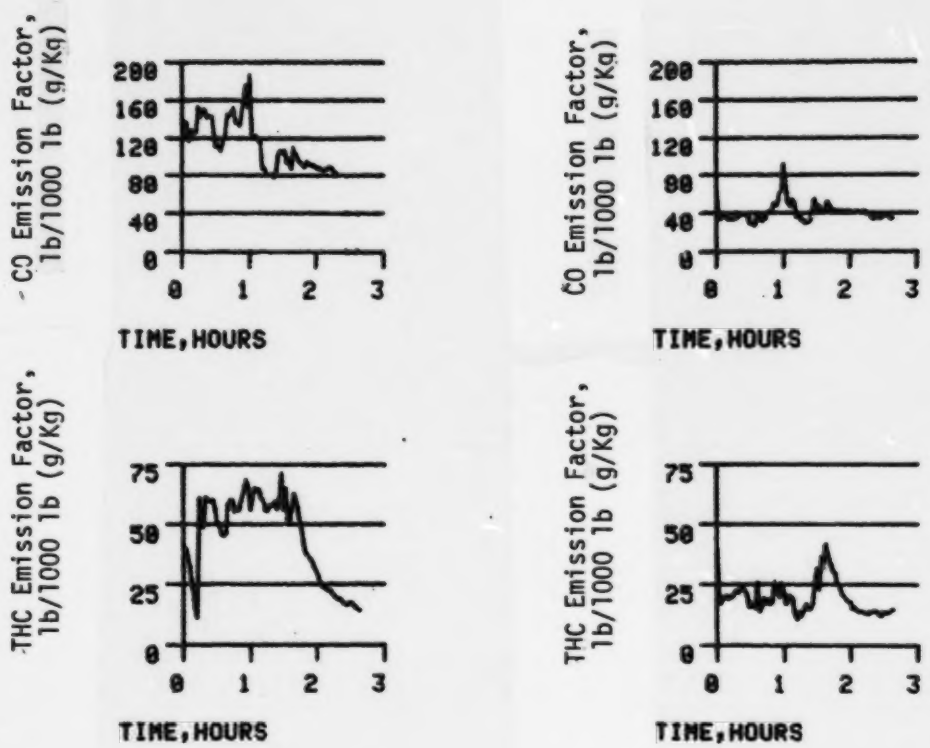


FIGURE 3. Emission Factors with Active Catalyst-Test 5

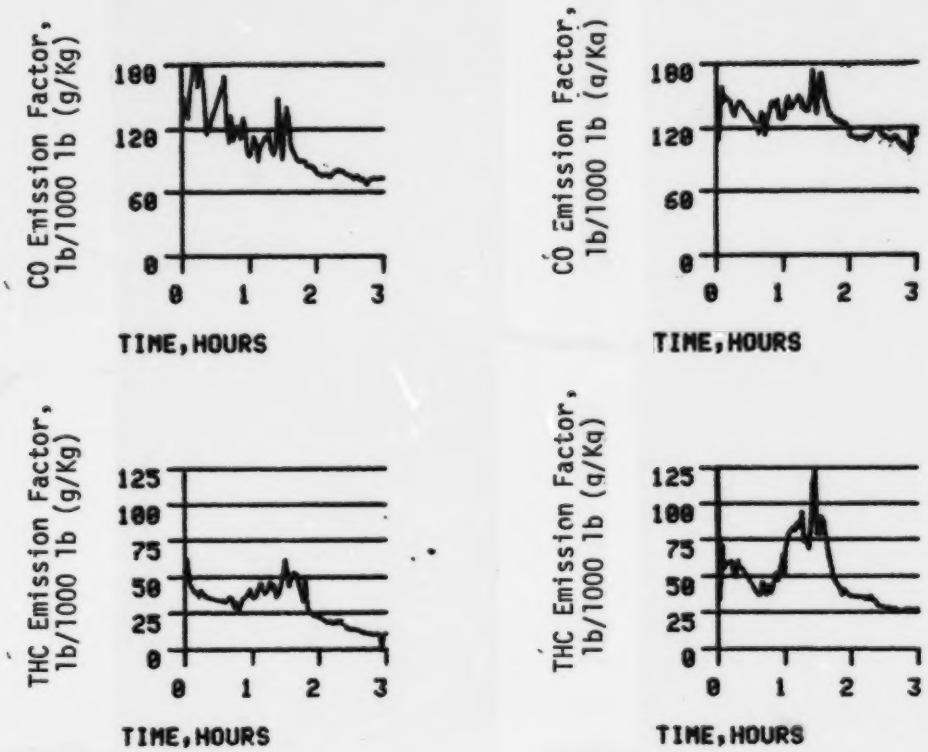


FIGURE 4. Emission Factors with Inactive Catalyst-Test 6

(at 0 percent O_2) for two of the tests are shown in Figures 5, 6, 7, and 8. Any difference between NO and NO_x is assumed to be NO_2 which is negligible in these test results. The observed increase in NO/NO_x is apparently NO, but the reason for the increased NO concentrations after the catalyst (both active and inactive) is unknown. Both the magnitude of increase and the overall concentration were higher in the active catalyst burn than in the inactive catalyst burn.

Grab Sample Results

The composition of volatile gases are summarized in Table 4. Test 6 was made with a blank catalyst and clearly shows the effect of the catalyst during tests 1 through 4. Without the catalyst higher concentrations of carbon monoxide, hydrocarbons, and hydrogen were found. Also elevated benzene levels were found in the blank run. Benzene and ethanol are not gases at room temperature and atmospheric pressure, therefore these data are approximate amounts and the true concentrations may be much higher. All results are reported on a dry basis.

The mass spectra were searched for key masses that might indicate the presence of acetic acid, propionic acid, toluene, acetaldehyde, and other low molecular weight compounds, but they were not detected. Some compounds of interest which could not be assigned by gas mass spectrometry due to interfering masses were nitrogen oxides, formaldehyde, and ammonia.

No sulfur gases were detected, and the "less than" values indicate the lower limit of detection. This is also true of "less than" elsewhere in Table 4. An unknown compound representing approximately 0.03 volume percent is present at mass 30 in all samples analyzed by the mass spectrometer. This could be nitrogen oxides, or a contribution from formaldehyde, but it could not be identified.

Results of Total Organics Determinations

The Modified Method 5 train provides a measure of total organic emissions. The protocol for analyzing the train components was discussed in the experimental section of the report and results of extractable organics analyses (GRAV) and semivolatile organics analyses (TCO) are given in Table 5. It is surprising that the blank catalyst had equivalent organic levels to the active catalyst runs.

These data indicate that the noble metal catalyst is most effective with volatile species. The results presented here also indicate that semivolatile organics constitute a lower total fraction of flue gas from wood stove combustion than either the volatile organics or high molecular weight organics (bp 300 C). This effect is shown stylistically in Figure 9. If additional research confirms this effect, noble metal catalysts are most effecive on volatile organic emissions. The particulate portion and higher molecular weight species found in wood smoke are not reduced an equivalent amount. The results for PAH analyses in the next section also showed litle difference between the measured amounts of high molecular weight PAH compounds from active and inactive catalyst runs.

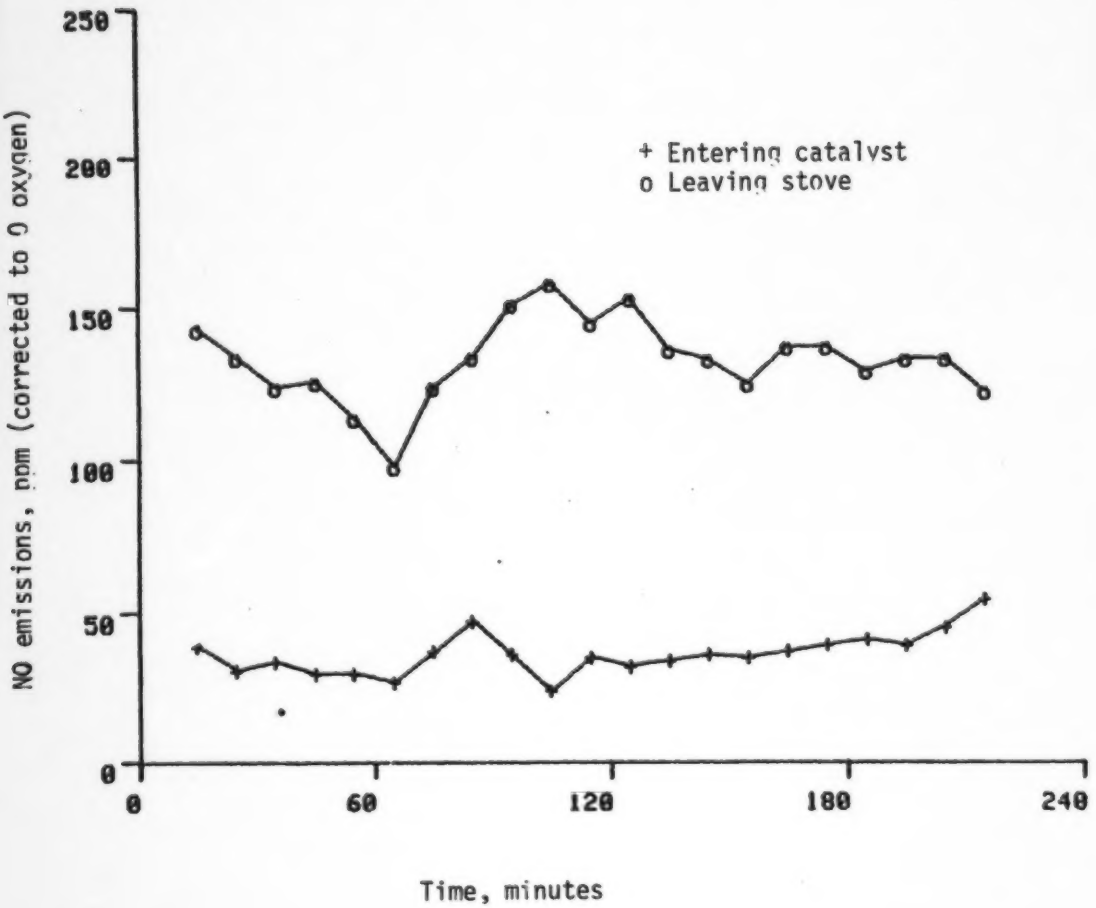


FIGURE 5. NO Emission with Active Catalyst-Test 5.

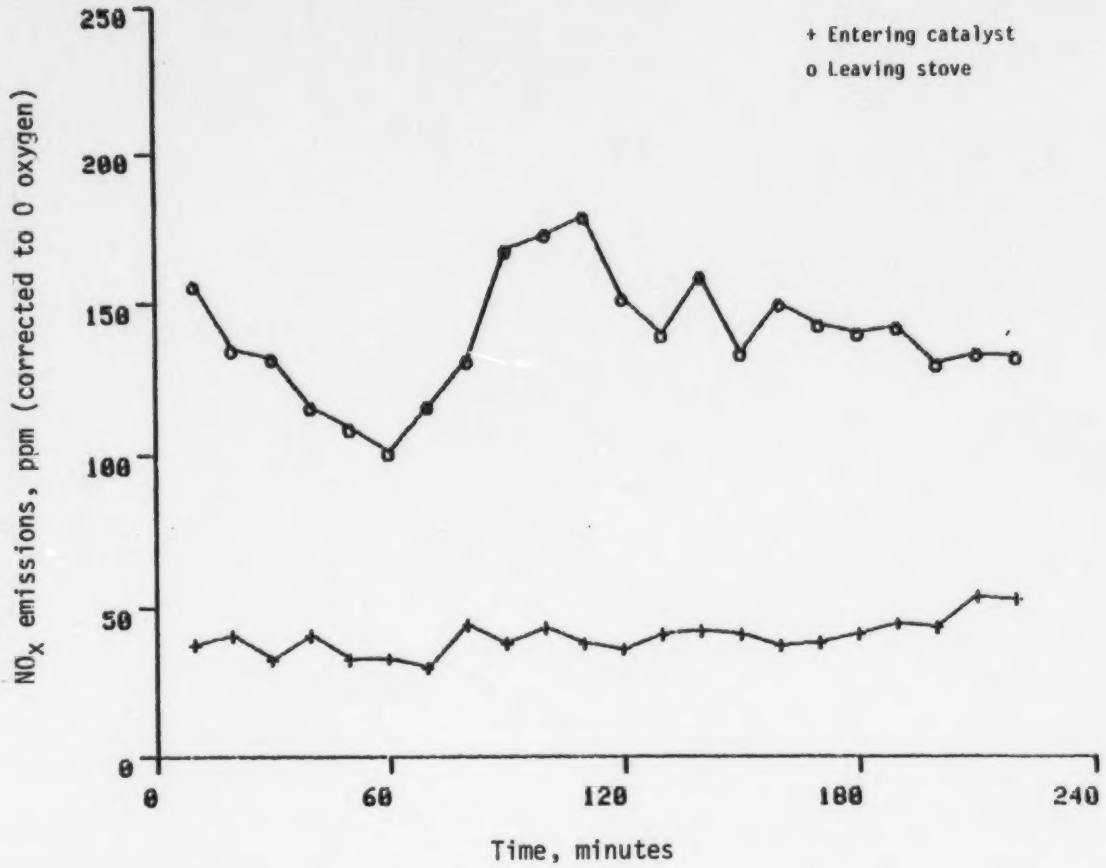


FIGURE 6. NO_x Emissions with Active Catalyst-Test 5.

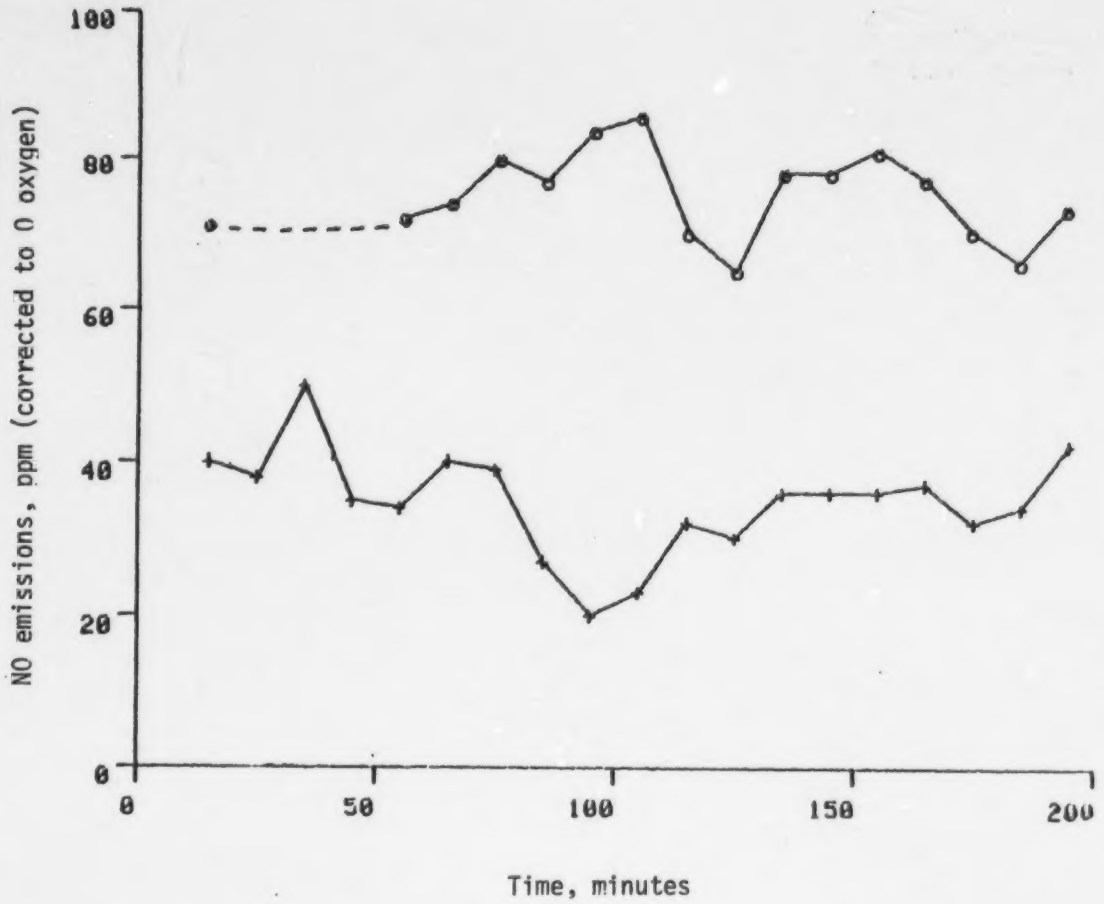


FIGURE 7. NO Emissions with Inactive Catalyst-Test 6.

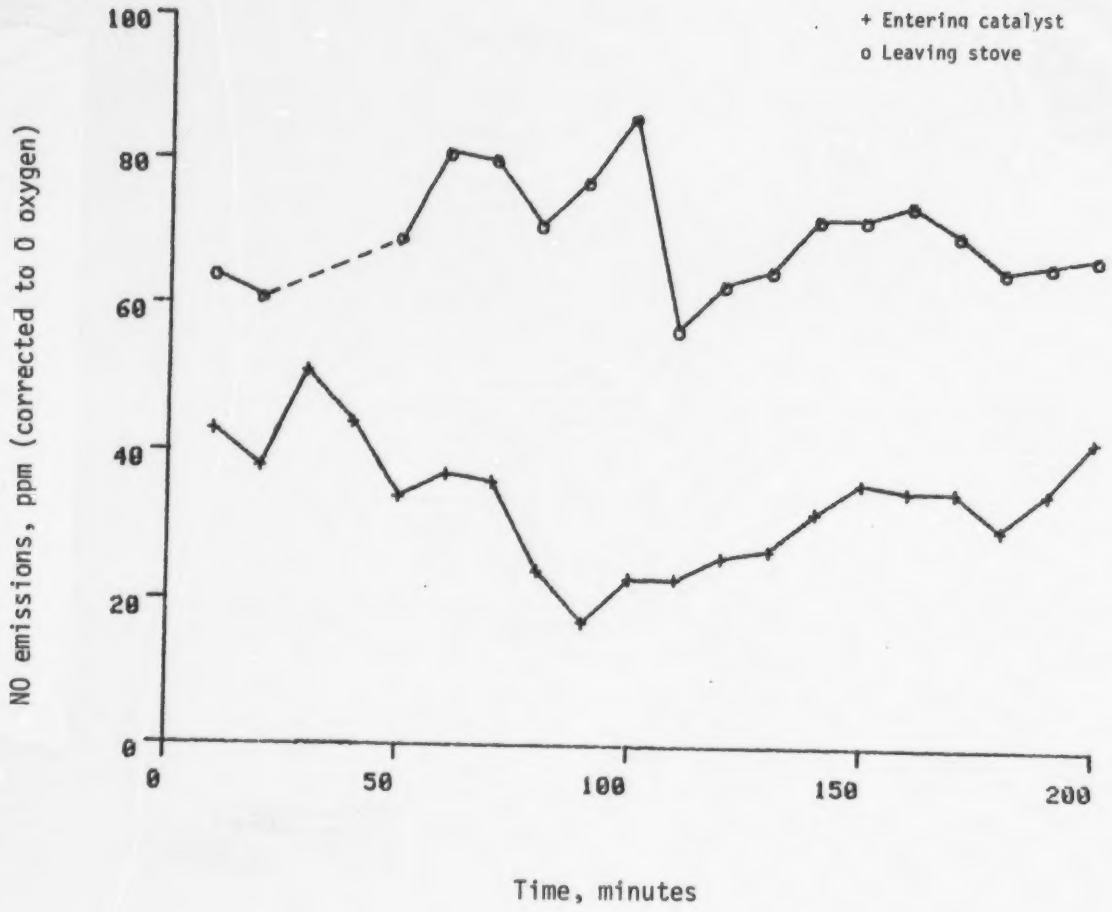


FIGURE 8. NO_x Emissions with Inactive Catalyst-Test 6.

TABLE 4. VOLATILE FLUE GAS COMPOSITION

Test No.	1	2	3	4	6	Instrumental Reproducibility
	Volume Percent (Dry Basis)					
Nitrogen	77.3	77.2	77.4	77.5	76.5	± 0.2
Oxygen	14.1	8.85	13.8	12.0	10.1	± 0.1
Carbon dioxide	7.11	12.5	7.46	9.17	10.1	± 0.05
Carbon monoxide	0.35	0.38	0.20	0.25	1.30	± 0.03
Argon	0.94	0.94	0.94	0.95	0.94	± 0.02
Methane	0.13	0.09	0.15	0.07	0.16	± 0.03
Ethanol*	0.03	0.01	0.01	0.01	0.03	± 0.01
Hydrogen	0.05	0.05	0.05	0.05	0.15	± 0.05
Benzene	0.01	0.01	0.01	0.01	0.02	
	Parts Per Million By Volume					
Ethylene, or acetylene	200	214	175	149	732	± 10
Ethane	115	50	100	51	117	± 10
Propylene	20	18	22	14	45	± 5
Propane	17	0.2	12	4	45	± 1
Unknown #1**	2	18	13	1	4	
Unknown #2	2	1	1	1	2	
Unknown #3	45	20	25	17	39	
1-Butene	11	1	1	1	9	± 2
n-Butane	1	1	1	1	1	
Hydrogen sulfide	0.5	0.5	0.5	0.5	0.5	
Carbonyl sulfide	0.5	0.5	0.5	0.5	0.5	
Carbon disulfide	0.5	0.5	0.5	0.5	0.5	
Sulfur dioxide	1	1	1	1	1	

*Primarily ethanol.

**Calculations based on normal sensitivity.

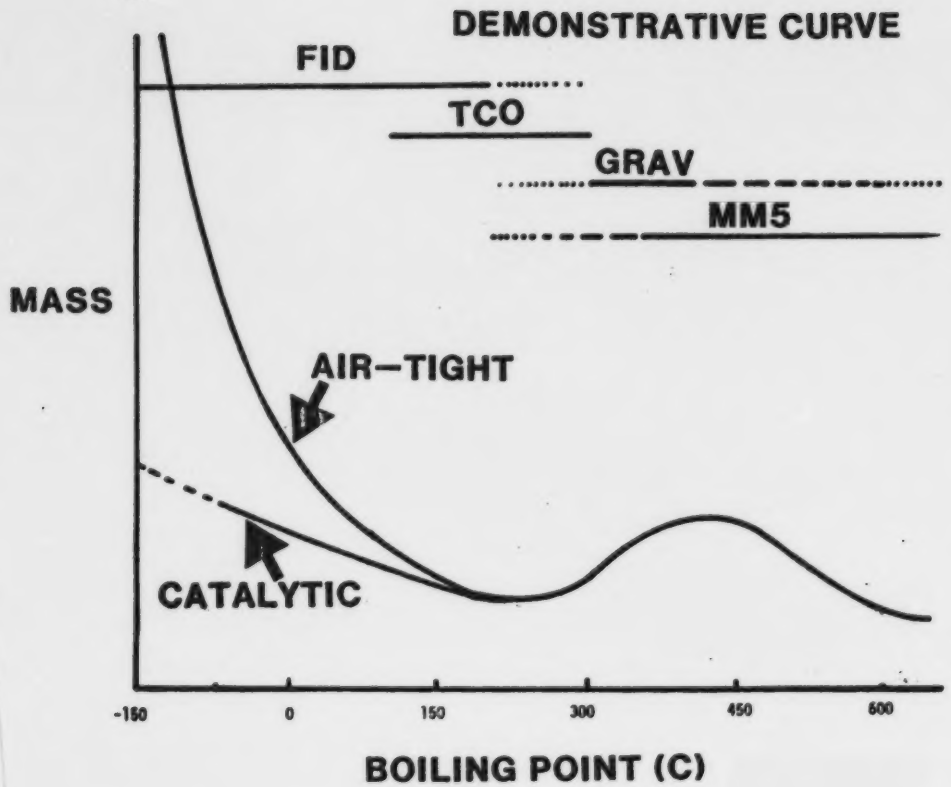


FIGURE 9. Characterization of Samples by Boiling Point.

TABLE 5. TOTAL MEASURED ORGANIC EMISSIONS

	Relative Burning Rate	Test No.	GRAV (mg/m^3)	TCO (mg/m^3)	Total (mg/m^3)	Total (g/kg)
	medium	2	413	1.9	415	3.75
	very low	3	382	3.1	385	5.82
	low	4	167	0.96	168	5.63
Average with Catalyst	low	Av	321	2.0	323	5.07
Blank Catalyst	very low	6	328	3.3	331	7.62

Results of PAH Analyses

A reconstructed ion chromatogram is presented in Figure 10 which shows the complexity of peaks observed in this type of sample. The individual compounds were analyzed by reverse search, mass spectral matching with quantification performed using a reference internal standard (9-phenylanthracene). Area counts were taken from the principal fragment of each PAH compound analyzed and a calibration curve was constructed for each compound using a synthetic standard mixture.

A representative group of indicator PAH compounds were used to characterize the emissions of these compounds. The results of these analyses are shown in Table 6. As these data show, most PAH compounds were lower in the active catalyst tests; however the blank catalyst registered the lowest PAH levels for several compounds. Since all four tests were at low burn rates it is evident that the blank catalyst may have a significant catalytic activity. Also it should be noted that these data are corrected for the system blank but not for recoveries. An isotopically labelled recovery standard, d_{12}-benzo(a)pyrene, was added to the resin catch of each MM5 train after sampling and the amounts of d_{12}-BaP measured was used to indicate losses through workup, handling, and analysis. The measured recoveries are shown as percentage of the spiked standard (d_{12}-BaP) in Table 7. Besides the variability observed in the active catalyst data, the active catalyst tests show generally higher PAH levels than the blank catalyst test.

These tests were all low burning rates where highly erratic combustion and variable stack flow behavior was observed. One can draw from these data that emission factors for wood stoves with catalyst assisted combustion are difficult to define at very low burning rates.

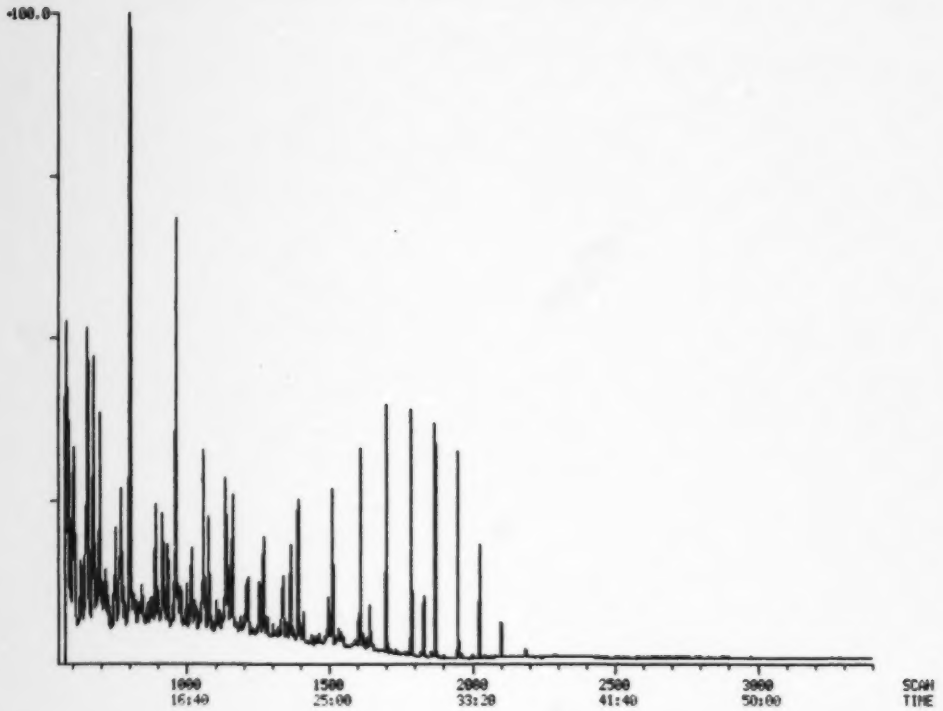


FIGURE 10. Total Ion Chromotogram of Flue Gas.

TABLE 6. INDIVIDUAL PAH COMPOUNDS ($\mu g/m^3$)

Test No.	Active Catalyst			Blank Catalyst
	2	3	4	6
Relative Burning Rate	medium	very low	low	very low
Naphthalene	960	960	550	520
Acenaphthene	52	52	29	36
Acenaphthylene	560	560	270	610
Fluorene	160	160	94	26
Phenanthene	630	630	370	790
Anthracene	73	70	62	96
Fluoranthene	190	190	100	270
Pyrene	200	200	96	220
Benzo(a)anthracene	66	66	39	68
Chrysene	49	49	26	53
Benzo(k/b)flouranthene	85	85	60	104
Benzo(e)pyrene	69	69	45	63
Benzo(a)pyrene	77	81	56	82
Perylene	41	41	37	36
Indeno(1,2,3,-c,d)pyrene	70	59	70	69
Benzo(g,h,i)perylene	59	59	48	52
Anthanthrene	60	60	41	48
Coronene	--	--	49	45
Total of above	3401	3391	2042	3188

TABLE 7. RECOVERY STANDARD DATA (d_{12}-BaP)

Test No.	Active Catalyst 2	3	4	Blank Catalyst 6
Fraction Recovered, percent	45	47	50	82

Benzo(a)pyrene (BaP) is a convenient compound for comparing relative PAH emissions measured by other researchers. Relative BaP levels for four tests are given in Table 8. These results are compared with BaP results recently reported by TVA researchers who measured PAH emissions from both catalyst assisted and airtight wood stoves[2]. As these data show, the results of this study are consistent with the TVA results and both catalyst wood stove studies, this investigation and the TVA research program, found lowered PAH levels using active, noble metal coated catalysts to assist wood combustion.

TABLE 8. BENZO(a)PYRENE RESULTS FROM CATALYTIC WOOD STOVE STUDY

Units	Test No. 2	3	4	6(1)	Catalyst(2) Stove (TVA)	Airtight(2) Stove (TVA)
Gas Based Units (mg/m^3)	0.077	0.081	0.056	0.082	0.053	--
Fuel Based Units (mg/kg)	0.70	1.2	1.9	1.9	0.5	14.2
Thermal Based Units (pg/J)	35	61	94	95	25	--

(1) Blank catalyst test.

(2) These values contain both benzo(a)pyrene and benzo(e)pyrene measurements, see Ref. 2.

SECTION 4

DISCUSSION OF TEST RESULTS

The wood combustion process is generally characterized by initial fast surface combustion in which moisture and organic pyrolysis products are evolved, during which an outer char layer is formed. During the middle portion of the typical wood burning cycle, pyrolysis products are evolved. Slow burning takes place in this portion of the burn with pyrolysis products and interior moisture passing through the char layer simultaneously. Late in a typical burn, residual fuel is essentially all char; therefore, hydrocarbon emissions are very low and surface burning takes place. The organic emissions, which are products of incomplete combustion generally are more concentrated during the early portion of a test burn.

These effects are observed by examination of the emission factors shown in Figures 2, 3, and 4. Pyrolysis products as shown by THC emissions usually have initial high values early in the test and lower values as the wood becomes charred. Irregularities are presummably associated with shifting wood and inherent irregularities within the pieces of wood.

Effect of Stove Operation on Combustion

The operation of a wood heating appliance is generally performed at a fixed rate of combustion air, although thermostatically controlled air dampers are available. The effect of decreasing pyrolysis and combustion rates during the burn cycle results in (1) increasing excess air levels and (2) decreasing combustion gas temperatures. These are compound effects since increased excess air contributes a thermal dilution to the combustion gas temperature. This effect can be observed in Figure 11 where excess air and combustion gas temperatures are plotted relative to time.

The stove as received from the supplier had an unusually low resistance to flow of secondary air as it was supplied directly to the entrance of the catalyst. No controls were provided on this stove for secondary air regulation, although controls for primary air were provided by a damper in the door. This secondary air flow phenomenon, together with the deliberately low primary air flow employed, resulted in higher excess air rates at the catalyst than might have been preferred at the desired low burning rates. The severity of this effect is related to both the burning rate and to the draft supplied by the chimney in any installation.

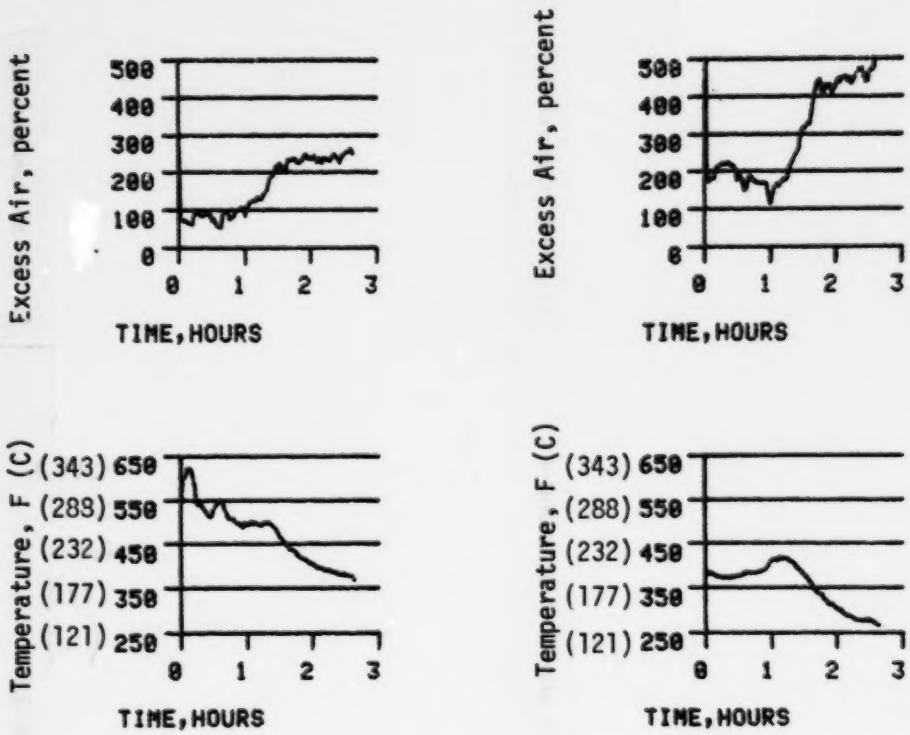


FIGURE 11. Excess Air and Flue Gas Temperatures with Active Catalyst-Test 5.

Catalyst Performance

With a catalytic convertor mounted in the stove the catalyst bed heats up very quickly, and as it reaches about 260 C (500 F), the catalytic action becomes effective and secondary combustion is started. Even when the gas temperature entering the catalyst goes slightly below 260 C (500 F), the catalyst is still effective and maintains ignition with at least partial burning of the combustible material. Figure 11 shows a typical test with peak temperatures for gas leaving the burning wood at about 315 C (600 F) as they enter the catalyst. This temperature falls off throughout the remainder of the burn reaching a temperature just above 175 C (350 F) at the end of the test burn. This is referred to as the primary gas flow and it is subsequently mixed with heated secondary air upon entering the catalyst. Figure 12 shows the typical catalyst temperature over a burn cycle. These temperatures rise after heated air is added to the primary combustion products, and secondary combustion begins. This temperature goes much higher and stays high throughout about two thirds of the test period indicating active catalytic combustion.

When the catalyst was replaced by an identical ceramic substrate that had not been treated by the addition of the catalyst surface, the early temperatures were slightly lower and the blank catalyst temperature dropped to a lower value late in the test run. Figure 12 shows the differences dramatically, the upper curve obtained with the activated catalyst, the lower curve being obtained with the blank catalyst.

Effect of Catalytic Action on THC and CO Emissions

The promotion of secondary combustion by catalytic activation of combustion products can be initiated at temperatures around 260 C (500 F). The measured effect on emissions is a reduction in THC and CO levels measured before and after the catalyst. Figure 13 shows the effect of the catalytic action on hydrocarbon emissions. Emissions are reported in pounds of total hydrocarbons per thousand pounds of wood burned. Therefore, the hydrocarbon concentrations going into the catalyst as shown on the upper curve and the hydrocarbon emissions leaving the stove as shown on the lower curve are normalized to the same reporting units. There is a significant reduction in hydrocarbon emissions through two-thirds of the burn period using an active catalyst. After that period, presumably the wood has been reduced to char, and burning after that point has low hydrocarbon emissions. These data correspond to hydrocarbons with boiling points less than about 177 C (350 F). Total hydrocarbon data are measured in the FID as methane equivalents and are not absolutely quantitative. They do represent valid comparative values for the purpose of evaluating catalyst performance.

CO emissions are also effectively reduced by catalytically initiated combustion. In most cases, CO emissions downstream of the catalyst were 30 to 50 percent of the emissions entering the catalyst (Figures 2 and 3). Neither CO nor THC emissions were significantly reduced in the one test which used an inactive catalyst, (Figure 4).

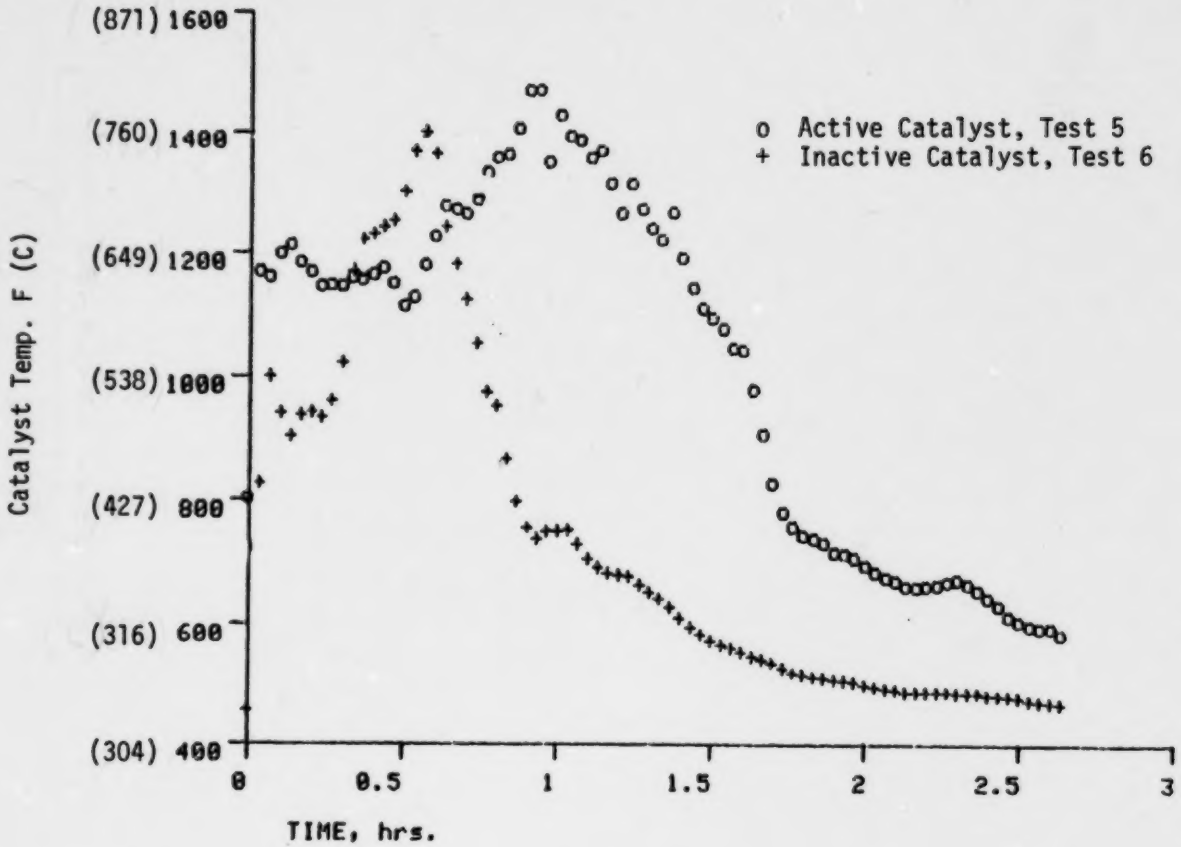


FIGURE 12. Temperatures Within Catalyst.

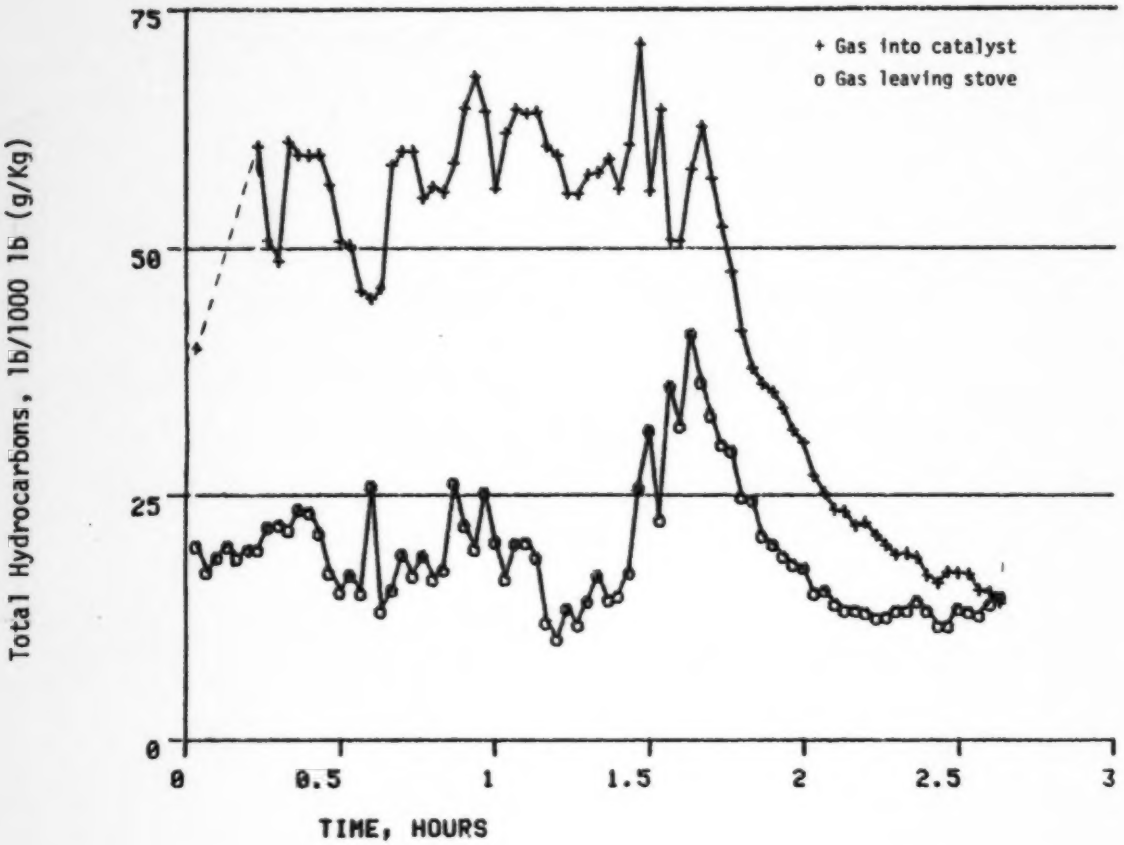


FIGURE 13. Hydrocarbon Emission Rates with Active Catalyst-Test 5.

The effect of the catalyst on the combustion of THC and CO can be illustrated by comparing the parametric THC and CO plots of emission factors for primary (before catalyst) and secondary (after catalyst) concentrations shown in Figures 14 and 15. These data are plotted on identical scales and thus the shift towards the common origin inidicates that both THC and CO are effectively reduced by catalytic combustion.

A similar plot (shown in Figure 16 with a different scale for THC) for secondary emissions from the inactive catalyst test indicates that emissions of both THC and CO are greater than from the active, catalyst-equipped appliance. Generally, emission factors for the inactive catalyst show little change between secondary and primary gas streams except that high CO emissions are reduced in the inactive catalyst.

In examining the effectivess of the catalyst in reducing CO and THC, two combustion processes must be considered: first the catalytic surface reactions which are diffusion limited (for hydrocarbons the assumed reaction is directly to CO_2 and H_2O without formation of CO[3]), and second, the gas phase reactions which are kinetically limited and are assumed to react by oxidation to CO, H_2O and H_2, followed by downstream conversion to CO_2 and H_2O. Therefore, the existence of CO in the catalyst outlet is evidence of gas phase reactions. In a catalytic equipped appliance the suspected reaction is surface catalysis of hydrocarbons and gas phase reaction of CO emissions. An unknown effect in wood combustion is the action of the catalyst on hydrocarbons with oxygen containing substituents such as aldehydes, ketones, phenolic groups and hydroxy groups. For most oxygenated compounds, bond energies would indicate that the CO group would be eliminated and then oxidized to CO_2 by gas phase reactions.*

To investigate these reactions, parametric plots of the THC and CO emission factors versus catalyst temperature were prepared for both an active catalyst test and an inactive catalyst test. Effects of the catalyst on CO emission factors are shown on Figure 17. The active catalyst was evidently very effective in reducing CO emissions in these two test burns, which were comparable except for catalyst activity. Similarly, Figure 18 shows that the active catalyst was also effective in reducing hydrocarbon emissions. In examining these figures, the low emission factors at low catalyst temperature should be ignored. These data, taken below 425 C (800 F) for the active catalyst and below 315 C (600 F) for the inactive catalyst, represent the burn periods at the end of the test burn when hydrocarbon and CO emissions are normally low and gas temperatures entering the catalyst are low. The indicated trends of these graphs would suggest that CO is unaffected by catalyst temperature except for a possible upward swing at the highest catalyst temperatures. CO reactions occur predominantly in the gas phase provided ample secondary air is available. The possible increase in CO at the highest catalyst temperatures may be an indication of oxygen cleavage but this could not be confirmed by the measurements in this program.

---

* The H_f for C=O of aldehydes is 176 Kcal/mole while C-C is 82.6 Kcal/mole, C=C is 145.8 Kcal/mole and C=H is 98.7 Kcal/mole based on polyatomic molecules at 25 C.

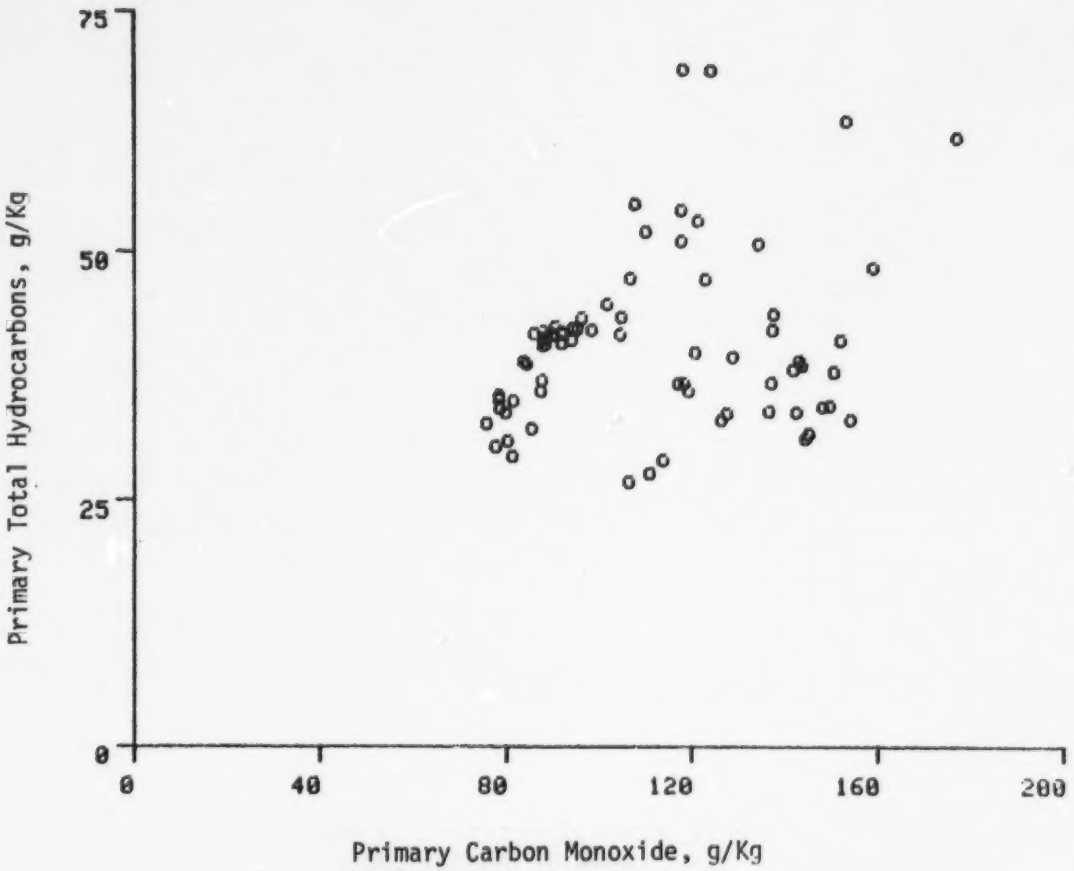


FIGURE 14. Total Hydrocarbon-CO Correlation for Gases Entering Catalyst-Test 5.

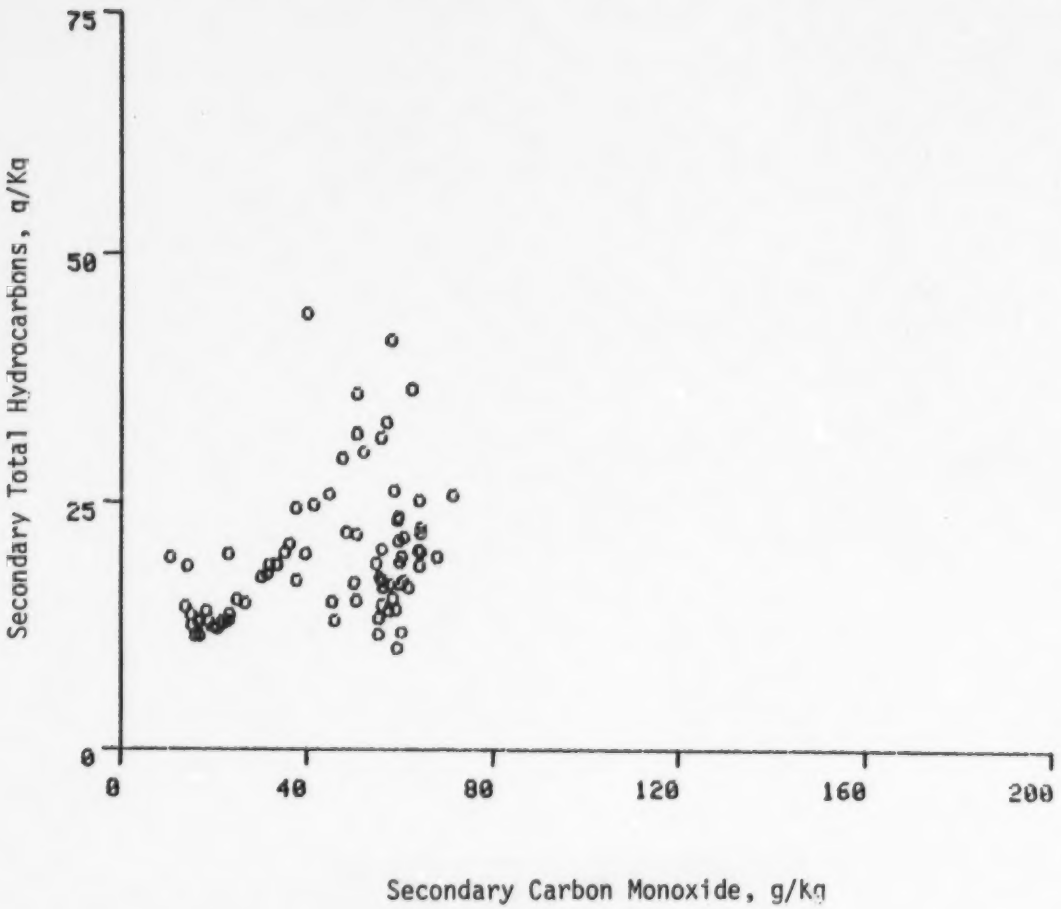


FIGURE 15. Total Hydrocarbon-CO Correlation for Gases Leaving Stove With Active Catalyst.

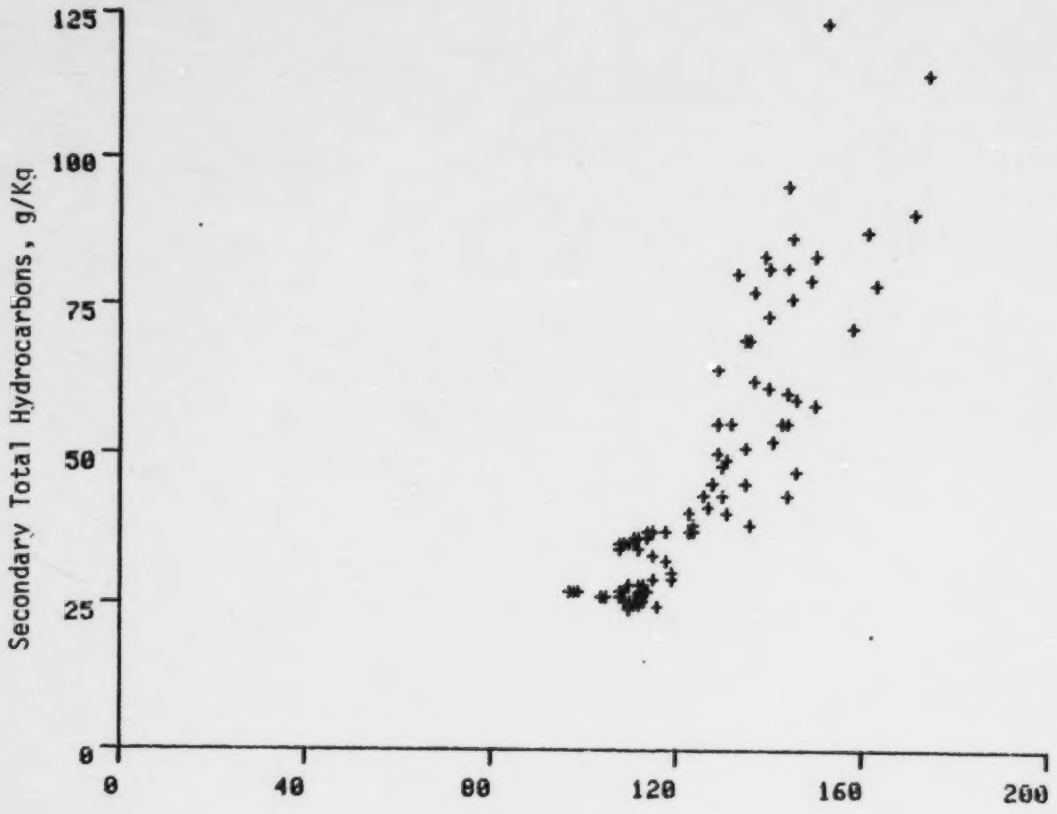


FIGURE 16. Total Hydrocarbon-CO Correlation for Gases Leaving Stove With Inactive Catalyst-Test 6.

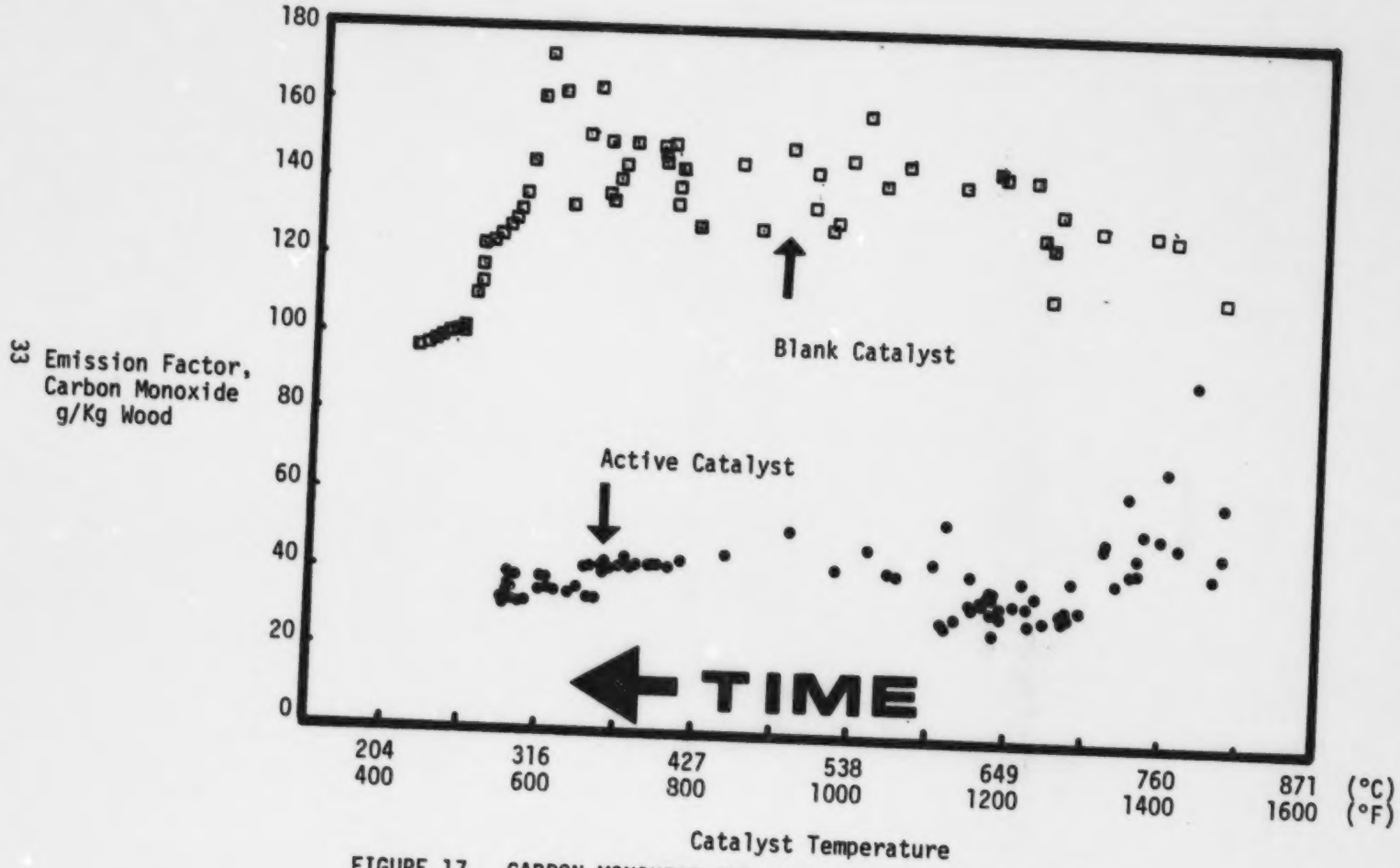


FIGURE 17. CARBON MONOXIDE EMISSION FACTORS CORRELATED WITH CATALYST TEMPERATURES

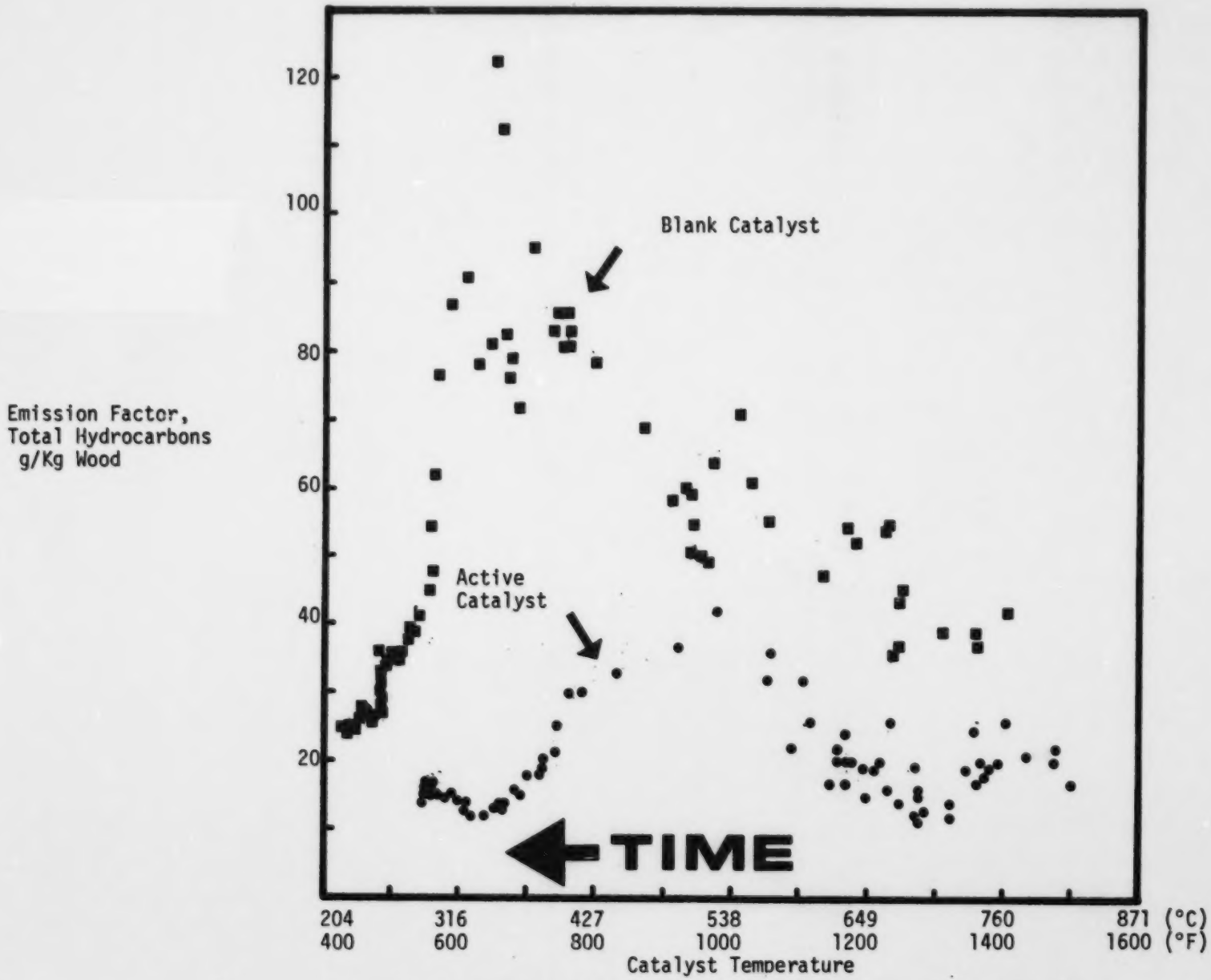


FIGURE 18. HYDROCARBON EMISSION FACTORS CORRELATED WITH CATALYST TEMPERATURES

THC emissions show a definite inverse correlation with catalyst temperature for both the active and inactive catalyst. This response for both substrates is not surprising since increased substrate temperatures were observed in both cases. The significance of THC plots is in regard to the frequency of the number of data points observed between the two tests. In the case of the active catalyst, a far greater number of low THC, high catalyst temperature points occurred, indicating that the sustained high temperatures observed in the catalyst measurements is responsible for the overall reduction in THC emissions. The effect of an active catalyst is thus to sustain the surface reaction of THC oxidation during conditions which would not normally combust THC in a conventional appliance.

Effect of Catalyst on NO_x

The observed results of NO and NO_x sampling were presented in Section 3. The surprising observation is made that gases leaving the stove were appreciably higher in nitrogen oxides than gases entering the catalyst unit, and this difference was maintained throughout the test burns.

In the inactive catalyst test, as with the activated catalyst, the emissions were appreciably higher leaving the catalyst than they were entering the catalyst. These data have been normalized to zero oxygen content so they can be directly compared. NO_x leaving the stove throughout this test program was approximately twice the NO_x entering the catalyst.

The NO_x was primarily NO both before and after the catalyst. The NO_2: NO_x ratio was approximately 0.1 at both locations, although exactly simultaneous measurements were not obtained.

Effect of Catalyst on Volatile Gases

Grab sample data for volatile gas characterization clearly display some of the chemical changes caused by the catalyst in this wood burning stove. The most pronounced changes in composition due to the catalyst are shown by the higher carbon monoxide, light hydrocarbons, hydrogen, and benzene levels found with the inactive catalyst. Overall, the inactive catalyst results indicate that hydrocarbons emissions in the lighter fractions are significantly higher than in tests with the active catalyst. This conclusion supports the reported differences observed for total hydrocarbon monitoring.

Effect of Catalyst on Condensibles and Particulate

In this program measurements of particulate and condensable hydrocarbons were obtained from the Modified Method 5 train samples described in Section 2. The overall emission results are presented in Table 9 as four measurements: (1) particulates collected on the probe and heated filter, (2) condensible organic compounds with boiling point greater than about 300 C, (3) total chromotographable organics (TCO) compounds with boiling points between 100 C and 300 C, and (4) the average Total Hydrocarbon Concentration (THC), as measured by the on-line FID.

TABLE 9. PARTICULATE AND ORGANIC EMISSIONS .

Test No.	Excess Air, percent	Particulate (mg/scm)	Grav. (mg/scm)	TCO (mg/scm)	THC ppm
2	75	30.9	413	1.9	--
3	200	36.6	382	3.1	1001
4	570	17.4	167	0.96	2184
6	360	14.7	328	3.3	3186

The results are surprising in that with the exception of Test 4 the higher molecular weight organics appear to be nearly equivalent. Test 4 represented a medium air setting with a low burn rate, and apparently produced the lowest level of total hydrocarbons (and also CO, see Table 3). The results from these tests indicate that the catalyst may not be as effective in reducing the higher molecular weight organics as in reducing the lighter organics. Therefore, if light organics are the predominant pyrolysis products, catalytic combusiton proceeds rapidly and efficiently, but the heavier organics formed during pyrolysis may not be as efficiently combusted by the catalyst.

As indicated on Table 3, Tests 4 and 6 had much higher oxygen concentrations in the flue gas, indicating high excesss air levels and associated dilution of the particulate and organic emissions.

SECTION 5

RECOMMENDATIONS FOR FUTURE TEST PROGRAMS

Recommendations for additional tests to characterize catalyst performance more thoroughly include the following:

- Verification of the observed increase NO_x with the use of catalysts.
- Operation with lower flow rates of secondary air into the appliance.
- Evaluation of gas phase reactions in secondary combustion both as a function of temperature and time.
- Determination of the distribution of light to heavy hydrocarbons species in emissions and the effect of catalyst induced reactions on species formed.

REFERENCES

1. Cooke, M., J. M. Allen, C. V. Knight, M. S. Graham, D. K. Knight, and D. W. Kuberg, "Method for Sampling and Analysis of Organic Emissions from Residential Wood Combustion", Presented at the National American Chemical Society Meeting, September 14, 1982.

2. Knight, C. V. and D. K. Knight, presented at the A.P.C.A. Specialty Conference on Measurement and Monitoring of Non-Criteria (Toxic) Containments in Air, Chicago, IL., March 22-24, 1983.

3. Barnes, R. H., M. J. Saxton, R. E. Barrett, and A. Levy, "Chemical Aspects of Afterburner Systems", EPA-600/7-79-096 U.S. Environmental Protection Agency, Research Triangle Park, NC, 1979, 95 pp NTIS PB 298 465/6.